Theoretical Investigation of the Structures and Dynamics of Crystalline Molecular Gyroscopes

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論 文 内 容 要 旨

The crystalline macrocyclic compounds with bridged π-electron systems have received much attention in terms of their unique structures, dynamics and functions. In particular, the phenylene-bridged macrocages whose interior rotator (phenylene) is protected by an exterior framework (stator) are structurally analogous with the macroscopic gyroscope and are expected to have many useful collective effects and properties in the crystal. Recently, Setaka et al. have reported an X-ray crystallography of the molecular gyroscope that has phenylene rotator encased in three long siloxaalkane spokes. They found three equilibrium positions of the phenylene rotator around the molecular axis, suggesting that the rotary motion among the three equilibrium positions exhibits various functions expected as a crystalline molecular gyroscope.

We theoretically investigated the molecular structures and rotational dynamics of this novel molecular gyroscopes by applying cheap yet decent theoretical methods namely non-self-consistent-charge (NCC)- and the self-consistent-charge (SCC)- density functional based tight binding (DFTB). In order to get the reliable molecular structures, we also optimized the unit cell geometry by the Gaussian optimizer and then inserted the periodic boundary condition (PBC) with dispersion energy correction parameters in DFTB-input format by utilizing the "Gaussian-external" methodology. Prediction of the consistent molecular geometries with identical Si-O-Si angles of each siloxaalkane arm even after changing the optimization methodologies with different algorithms signifies the most reliable molecular structures. All the optimized unit cell geometries of the three stable molecular structures are found to be compatible with that of the X-ray crystallography. In order to confirm the sufficient "free volume" unit present around the rotator, we analyzed the available space that exists between the siloxaalkane spokes and the phenylene rotator of each optimized as well as X-ray geometry. No significant changes were noticed in the theoretically produced molecular structures. In terms of energies and stabilities, theoretically predicted most stable structure is found to be resembled well with the experimental observation. The highest energy structures are 0.48 and 0.60 kcal/mol and the second highest energy structures are 0.41 and 0.57 kcal/mol higher than the lowest energy structure as predicted by NCC-DFTB and SCC-DFTB methods respectively. Theoretically converged most stable (the lowest energy) structure has the phenylene angle $\sim 0.35\ \pi$ which is consistent with the experimentally observed lowest energy structure with the phenylene angle $\sim 0.55\ \pi$.

Prior to the calculation of the potential energy surface (PES) under PBC, the qualitative agreement of the DFTB methods was confirmed with that of the density functional theory DFT (B3LYP/6-31G**) calculations in reference to an isolated siloxaalkane molecular gyroscope. The "partial optimization method" of NCC-DFTB was applied to the 1,4-bis(trimethylsilyl) benzene (a reference molecule) and siloxaalkane molecules explicitly and found that the rotational energy barrier between them were incomparable to each other. We reasoned it

by saying that due to the absence of a shielding frame in the reference molecule, its phenylene ring becomes naked and hence highly exposes to the surrounding molecules that intensifies the intermolecular steric effect. The PES was also scanned by the DFTB-"full optimizations with constraints" method and predicted the activation height. But either of these methods could not locate the experimentally observed three stable positions of the phenylene upon π flipping.

Along with this discrepancy, the accurate computation of the rotational energy barrier was also very needful as its experimental value is still unavailable. For such purposes, we switched our PES scanning methods to Gaussian-external methodology. In this methodology, we directed the DFTB method under PBC via external script and achieved the PES that clearly displays the three stable positions of the phenylene ring upon π flipping. The PES is found to be asymmetric; that is why the phenylene rotator is expected to exhibit unidirectional motion. It is periodic in shape by π with respect to phenylene angular displacement. The rotational energy barrier of around 0.715 kcal /mol is estimated under PBC without dispersion corrections. The SCC-DFTB method with dispersion energy corrections revealed the similar features of the PES but slightly higher rotational barrier of ~1.144 kcal /mol. This is due to the inclusion of the van der Waals interaction between the rotator and the siloxaalkane spokes (and surrounding molecules). Meanwhile, the NCC-DFTB method was found to be unable to address the dispersion effects. It suggests that inclusion of the self-charge consistency is mandatory to include the much weaker van der Waals type interaction in electronic energy calculations. The appearance of such significantly low rotational barriers signifies the high degree efficiency of the encapsulating spokes to isolate the rotating units from the neighboring molecules. As far as we know, this is the lowest rotational potential energy barrier observed in the phenylene based molecular gyroscopes as the pioneer research group of Garcia-Garibay et al. is still unable to synthesize the molecular gyroscopes with rotational barrier less than 4.3 kcal/mol. In terms of implementing "free-rotor" concept in reality, the cage like structure of the siloxaalkane molecular gyroscope can be regarded as an exemplary model as the barrier experienced by its phenylene rotator is as large as the thermal energy at room temperature (~0.59 kcal/mol). This scenario acts as the key for developing barrier-less molecular gyroscopes. It implies us to conclude that developing highly efficient encapsulating frame around the rotating segment is the key step to model / synthesize highly functional molecular gyroscopes and for such systems, very weak van der Waals type interactions can be declared as a predominant factor for creating the flipping energy-barrier.

The MD simulations under PBC with and without dispersion energy correction show the notable indications of phenylene flipping at high and low temperatures. The van der Waals interaction makes the phenylene rotary dynamics slower due to much higher barrier felt by it. This is verified tentatively from our observation that time required to undergo π phenylene flipping in the presence of dispersion energy correction is >15 ps at 800 K whereas in without dispersion energy case, it takes < 15 ps at the same temperature. Similarly, on the way of its turning around, phenylene rotator finds several stops at different angular positions where it stays for several picoseconds. We analyzed all the stops and found that their corresponding angular positions are in reasonable agreement with the positions of local and global minima appeared at the PES. Moreover, we determined the flipping rates from the most stable to the second most stable position of the phenylene at 800 and 1200 K by applying Arrhenius equation and then estimated the E_a value to be ~0.73 kcal/mol. This value is in good agreement with the activation barrier height (~0.71 kcal/mol) calculated by the NCC-DFTB method without dispersion energy correction.

Although the DFTB approach to explore the geometries of large molecules and clusters or complicated solid state structures and to perform MD simulations of dynamical processes are not new, it provided us a superb theoretical description of the experimental observations of the crystalline molecular gyroscope. Obviously, in this study, the weakest point is the lack of dispersion constants of silicon atom, though the most suitable parameter set was used. The present study illuminates many aspects of rotational barriers and processes under PBC with and without van der Waals force of interaction, which are difficult to gauge experimentally. The most important conclusion of this work is that, in the presence of an efficiently encapsulating gyroscopic frame around the rotating segment, the rotary dynamics of the crystalline molecular gyroscopes can be highly improved (i.e. extremely low barrier). Understanding such microscopic mechanisms of rotations with the help of reasonably simple theoretical method could be highly beneficial for the development of nanodevices based on assemblies of molecular gyroscopes and ultimately becomes an indispensible tool for the molecular machinery world.

論文審査の結果の要旨

スポークと呼ばれる外部骨格とそれに保護された回転子（ベンゼン環など）からなる結晶分子ジャイロスコープ（分子ジャイロ）はその回転制御などによって分子デバイスとしての応用が期待されている。様々な分子ジャイロが合成されるようになり、その構造や機能に関して第一原理理論に基づいて定量的に評価することが求められるようになってきた。これにより、高機能分子ジャイロの設計・合成の指導原理を確立することができ、実験と理論が一体となった機能性分子結晶の研究分野が拓けていくはずである。Anant Babu Marahatta は、すでに合成されているベンゼン回転子を三本の長いシロキサアルカンのスポークで保護した分子ジャイロなどに対して（ベンゼンはシロキサアルカンのケイ素原子と単結合で架橋されフェニレン環となっている)、そのX線結晶構造を再現する電子状態計算法を確立し、回転子の回転速度を第一原理分子動力学計算によって明らかにした。本提出論文はその研究成果である。

第1章では、まず、分子ジャイロのこれまでの研究概要がまとめられている。特に、瀬高らによって合成されているシロキサアルカン分子ジャイロのX線結晶構造やその物性・機能が詳しく紹介されている。温度上昇とともに複屈折率が低下することがベンゼン環の回転によると説明されている。

第2章は、結晶性分子ジャイロを理論的に取り扱うための電子状態計算法とそれに基づいた動力学法の説明にあてられている。計算負荷が軽いながらも密度汎関数法（DFT）レベルの結果を再現できる密度汎関数緊密結合法（DFTB）の原理と応用が紹介され、周期境界条件を課することによって結晶であっても適用できることが述べられている。DFTB に基づいた動力学によって、ピコ秒からナノ秒の時間スケールの中で起こると考えられる回転子のダイナミクス（フリッピング）も議論することができる。

第3章では、DFTB を用いた計算結果とそれらに基づいた考察が展開されている。まず、シロキサアルカン分子ジャイロの単分子の構造に対して、DFTB 法がより精度の高い DFT 法の結果を再現することを確認している。次に、X線結晶構造解析から得られているシロキサアルカン分子ジャイロ結晶の回転子の3つの安定構造を DFTB 法が再現できることが示され、DFTB 法の有効性を明らかにしている。回転子とスポークの間に大きな空間が存在しうることも確認されている。また、分子動力学計算から回転子が3つの平衡構造の間を移動して回転することが見いだされている。動力学シミュレーションに基づいたアレニウスプロットから得られた回転子の回転障壁（~ 1 kcal /mol）は DFTB の構造計算から求められた値とほぼ等しかった。回転子の回転速度は NMR などの実験からは決定できていなかったが、常温で 5~10 ns^{-1} と高速に回転していることがわかった。また、結晶中の分子間に働く分散力のような分子間力も回転子の障壁を高める効果があり、回転子の動的制御を目指す上で重要な因子になり得ることがわかった。

第4章では、以上の成果がまとめられており、DFTB 法とその分子動力学が機能性分子結晶の研究に必要な精度と計算速度を有するきわめて有効な方法であると結論づけられている。

本研究によって、高機能のデバイスとしての可能性を秘めた新規分子ジャイロを理論的に設計する道が拓かれ、その先駆的な研究成果は高く評価される。以上、本論文は、本人が自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、Anant Babu Marahatta 提出の博士論文は、博士（理学）の学位論文として合格と認める。